This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

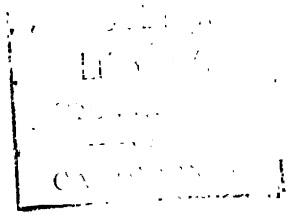
137
4S3

$B 242 484

CHEMICAL ANALYSIS OF LEAD AND ITS COMPOUNDS

SCHAEFFER
WHITE

Agric. Dept. Main Lib.



The Chemical Analysis of Lead and Its Compounds

JOHN A. SCHAEFFER, A. M., PH. D.
Chief of Laboratory and Director of Research

AND

BERNARD S. WHITE
Assistant Chemist

UNIV. OF CALIFORNIA

PICHER LEAD COMPANY
JOPLIN, MO. CHICAGO, ILL. NEW YORK, N. Y. PITTSBURGH, PA.

COPYRIGHT 1912

Main Lib.
Agric. Dept.

PICHER LEAD CO.
JOPLIN, MO.

PREFACE.

A review of the literature on the analysis of lead and its compounds reveals a multiplicity of methods, many of which are of little value in technical work of today, owing to the many operations entailed and the possibility of error attending every lengthy analysis. The laboratory of today, so closely connected with all lines of manufacture, must control through chemical analysis every process leading from the raw material to each finished product. It demands extreme accuracy coupled with rapidity of manipulation. That the best methods combining these salient points are not in general use in many laboratories dealing with lead compounds is evidenced from the numerous requests for such which continually reach us.

It is with the hope that the methods adopted by the leading laboratories in the lead districts, will prove of some special value, that this work is written. In it will be found certain new methods which retain exactness with considerable conservation of time and many others of general adoption. Should it aid in increasing the efficiency of any laboratory practice the authors will feel that its mission has been fulfilled.

August, 1912.

260272

CONTENTS.

Page

THE ANALYSIS OF LEAD ORES..... 7

THE ANALYSIS OF SUBLIMED WHITE LEAD.....15

THE DETERMINATION OF THE APPARENT DENSITY OF PIGMENTS 19

THE ANALYSIS OF SUBLIMED BLUE LEAD.....22

THE ANALYSIS OF RED LEAD AND ORANGE MINERAL..25

THE ANALYSIS OF FLAKE RED LEAD.....27

THE ANALYSIS OF LITHARGE.....31

THE ANALYSIS OF BASIC CARBONATE OF LEAD.....35

THE ELECTROLYTIC DEPOSITION OF LEAD.....44

THE ANALYSIS OF PIG LEAD..... 46

THE IODOMETRIC DETERMINATION OF ANTIMONY AND ARSENIC IN LEAD-ANTIMONY ALLOYS.....54

UNIV. OF
CALIFORNIA

ANALYSIS OF LEAD ORES.

The principal ore of lead which will be encountered by the analyst is Galena, the sulphide of lead, PbS. In certain instances Anglesite, the sulphate of lead, $PbSO_4$, and Cerrusite, the carbonate of lead, $PbCO_3$, will reach the laboratory for examination. The constituents usually sought in the analysis of these compounds are lead, zinc and silver, though at times the iron and silicates present must be determined. The value of the ore, however, will depend upon the content of lead, zinc and silver.

The ore upon reaching the laboratory is dried at 105°C for several hours and then pulped so as to pass through a 100 mesh sieve. The ore is then ready for examination.

Lead.

Digest one gram of the sample with 15 c.c. of concentrated nitric acid in a covered beaker. Boil the solution until the brown fumes of the oxides of nitrogen have disappeared. Add 6 c.c. of concentrated sulphuric acid and again boil until the heavy fumes of sulphuric acid are evolved. Allow the solution to cool, add 30 c.c. of water and boil. Remove the beaker from the hot plate and allow the solution to stand for from

three to four hours. Filter the solution, washing the precipitate by decantation three or four times to completely remove the iron. The filtrate is reserved for the determination of zinc.

Wash the filter paper used in the previous filtration with 75 c.c. of acid ammonium acetate solution made up in the following manner:

Ammonium hydroxide (concentrated)	200 c.c.
Water	225 c.c.
Acetic acid (80%)	250 c.c.

Follow this washing with 75 c.c. of hot water, allowing all the washings to be caught in the beaker containing the residual lead sulphate. Boil until complete solution has been effected and determine the lead volumetrically in the hot solution by titration with standard ammonium molybdate solution, as given under the Standardization of Ammonium Molybdate.

STANDARDIZATION OF AMMONIUM MOLYBDATE.

Dissolve 8.67 grams of ammonium molybdate in one liter of water. Each c.c. of this solution should be equivalent to one per cent of lead, when a one gram sample is used. Standardize with .2 gram of pure lead foil, pure lead sulphate or pure litharge. Dissolve the lead standard used in nitric acid, evaporate nearly to dryness, add

30 c.c. of water, then 5 c.c. of sulphuric acid, specific gravity 1.84, cool and filter. Dissolve the lead sulphate in 150 c.c. of acid ammonium acetate made up of the strength as above given. Dilute to 200 c.c. with hot water, boil and titrate with the standard ammonium molybdate, using an outside indicator of 1 part of tannic acid in 300 parts of water. The appearance of a yellow color indicates an excess of ammonium molybdate. It has been found that a correction of .7 of 1 c.c. of the titration volume must be deducted as a blank to allow for the sensitiveness of the reaction.

The following precautions must be observed in carrying out this method:

Calcium forms a more or less insoluble molybdate, and when calcium is present results are apt to be high. However, when less than 2 per cent of calcium and a high percentage of lead are present, there appears to be no interference from the calcium. This method is only applicable to samples containing more than 20 per cent of lead. Should a lower percentage of lead be present it may be determined by the bichromate method or weighed as the sulphate.

BICHROMATE METHOD FOR THE DETERMINATION OF LEAD.

Treat one gram of the sample with concentrated nitric acid, evaporate to dryness and cool. Take

up the residue with 75 c.c. of a solution made up in the following manner:

Acetic acid (80%)	255 c.c.
Ammonium hydroxide (concentrated)	150 c.c.
Water	595 c.c.

Boil gently for a short time, filter, and wash well with boiling water. Treat the filtrate with sufficient neutral potassium bichromate to precipitate all the lead, boil, filter and wash with hot water until all the uncombined potassium bichromate is removed. The above conditions must be carefully watched, as a slight deviation may result in the formation of a basic lead chromate. The ready formation of this compound has prevented the general adoption of this method. Dissolve the lead chromate in dilute hydrochloric acid (1:1), using as little of the acid as possible.

Titrate the chromic acid present in the solution with ferrous ammonium sulphate, having an iron value of .0025, using a two per cent. solution of potassium ferrocyanide as an outside indicator. It is necessary to deduct .5 of one c.c. of the ferrous ammonium sulphate for each 75 c.c. of solution used, as the amount required for the sensitiveness of the reaction.

Calculation.

The percentage of lead may be determined directly by dividing the number of c.c. of ferrous ammonium sulphate used by the factor 3.25. This factor is determined by the following equations:

$K_2Cr_2O_7 + 6\ Fe\ SO_4 + 8H_2SO_4 = 2KHSO_4 + Cr_2(SO_4)_3 + 3\ Fe_2(SO_4)_3 + 7\ H_2O.$

$2\ PbCrO_4 = 2\ Pb + Cr_2O_6.$

$Cr_2\ O_6$ is equivalent to 6 Fe.

2 Pb is equivalent to 6 Fe.

414 is equivalent to 336.

Factor from iron to lead equals 1.23.

Strength of solution equals .0025 Fe.

.0025 equals ¼ of .01%.

4.00 divided by 1.23 equals 3.25.

The number of c.c. of ferrous ammonium sulphate used divided by 3.25 gives the percentage of lead present when a one gram sample is used.

The lead may be calculated directly from the amount of iron titrated by using the factor 1.23.

SULPHATE METHOD FOR THE DETERMINATION OF LEAD.

Details for the gravimetric determination of lead as sulphate are given under the analysis of Basic Carbonate of Lead on page 35.

ZINC.

Add 8 grams of ammonium chloride to the filtrate and washings from the lead sulphate precipitate. Render the solution alkaline with am-

monium hydroxide, filter off any iron hydroxide which is precipitated, wash, dissolve this precipitate in dilute hydrochloric acid, reprecipitate with ammonium hydroxide, filter and thoroughly wash. Combine the filtrates, neutralize the ammonium hydroxide present with hydrochloric acid and add an excess of 6 c.c. of concentrated hydrochloric acid. Dilute to about 250 c.c., heat to about 80° C., add a small amount of sodium sulphite. Titrate with standard potassium ferrocyanide as outlined under the Standardization of Potassium Ferrocyanide, using as an outside indicator a 5% uranium nitrate solution.

STANDARDIZATION OF POTASSIUM FERROCYANIDE.

Dissolve 10 grams of pure metallic zinc in hydrochloric acid. The solution is made up to 1 liter and a volume equivalent to .2 gram is measured out. The remaining solution may be kept for restandardizing the ferrocyanide solution which, on standing, appears to change from time to time. In place of using the standard zinc solution, .2 gram of pure metallic zinc may be used for each standardization.

The ferrocyanide solution is made by dissolving 43.26 grams of crystallized potassium ferrocyanide and 7 grams of sodium sulphite in a liter of water. The addition of the sodium sulphite helps to keep the ferrocyanide solution at a constant strength. One c.c. of this solution will be equal to approximately .01 gram of metallic zinc.

The indicator is prepared by dissolving ura-

nium nitrate in water until a faint yellow color is produced. A 5% solution will usually give a good end reaction. A number of drops of this solution are placed on a spot plate, and the end point is determined by adding to each drop a few drops of the solution which is being titrated.

The acid solution containing .2 of a gram of zinc is made faintly alkaline with ammonium hydroxide, using litmus paper to determine the end point. Reacidify faintly with hydrochloric acid and add 6 c.c. of concentrated hydrochloric acid in excess. Dilute to about 250 c.c. and heat to about 80 degrees C.

The solution is titrated with the ferrocyanide solution until a few drops of the zinc solution give a brownish tinge to the uranium nitrate indicator on the spot plate. As the end point develops slowly, it is well to examine each spot after standing for a brief time. The first one developing a brown tinge is taken as the end point. It is necessary to make a correction for the amount of ferrocyanide solution required to develop a brown color in the uranium nitrate indicator when zinc is absent. This correction is deducted from the total amount of ferrocyanide solution used and will usually run about .5 of a c.c.

Silver.

The treatment of lead ores for the assay of silver depends wholly upon the nature of the

ore. The various fluxes used for the formation of the lead button cannot be outlined here, owing to their number; the analyst desiring to make this determination may readily determine a method of reduction by consulting any standard text on assaying. After the lead button has been obtained the silver may be determined as outlined under the Analysis of **Pig Lead.**

SUBLIMED WHITE LEAD.

(Basic Sulphate of Lead.)

An average approximate analysis of sublimed white lead as commercially placed upon the market should show about 78.5 per cent. of lead sulphate, 16 per cent. of lead oxide and 5.5 per cent. of zinc oxide. The percentage of sulphur dioxide present as an occluded gas, should not exceed .075 per cent., as a higher percentage of this gas causes a deleterious action on any oil in which this pigment is ground.

ANALYSIS.

TOTAL SULPHATES.

Mix .5 gram of the sample with 3 grams of sodium carbonate in a beaker. Treat the mixture with 30 c.c. of water and boil gently for ten minutes. Allow to stand for four hours. Dilute the contents of the beaker with hot water, filter off the residue and wash until the filtrate is about 200 c.c. in volume. Reject the residue. By this reaction all the lead sulphate is changed to carbonate, the sulphate being transposed into sodium sulphate, which is found in the filtrate.

Acidulate the filtrate with hydrochloric acid and add an excess of about 2 c.c. of the acid. Boil, and add a slight excess of barium chloride solu-

tion (12 c.c. of an 8 per cent. solution). When the precipitate has well settled, filter on an ashless filter, wash, ignite and weigh as $BaSO_4$. Calculate the $BaSO_4$ to $PbSO_4$ by using the factor 2.6, when a half gram sample is used.

Weight of $BaSO_4 \times 1.3$ equals weight $PbSO_4$.

On .5 gram sample factor $BaSO_4$ to $PbSO_4 =$ 2.6.

LEAD.

Molybdate Method.

Dissolve 1 gram of the sample in 100 c.c. of an acid ammonium acetate solution made up as follows:

Eighty per cent. acetic acid	125 c.c.
Concentrated ammonium hydroxide	95 c.c.
Water	100 c.c.

Add this solution hot and dilute with about 50 c.c. of water. Boil until dissolved.

Dilute to 200 c.c. and titrate with standard ammonium molybdate solution, spotting out on a freshly prepared solution of tannic acid. Details of this method are given under the Analysis of Lead Ores.

Ammonium molybdate is a slightly variable salt, but a solution containing 8.67 grams per liter usually gives a standard solution:

1 c.c. equals .01 gram Pb.

Standardize against pure PbO or pure $PbSO_4$.

Bichromate Method.

Treat the sample as above described until dissolved. If the solution is not quite clear, filter. Add to the filtrate an excess of neutral potassium biehromate solution. Boil and stand in a warm place until the precipitate has settled. Filter on a Gooch crucible, or weighed filter paper, wash thoroughly, ignite below a red heat and weigh as $PbCrO_4$.

The $PbCrO_4$ may be estimated volumetrically by titrating the chromic acid present. For this method, dissolve the lead chromate from off the filter with hydrochloric acid. Wash well and determine the chromic acid present with a standard solution of ferrous ammonium sulphate, using a dilute solution of potassium ferrocyanide as an outside indicator. The ferrous ammonium sulphate is made up of such strength that 1 c.c. will equal .0025 Fe. For a one gram sample divide the number of c.c. of ferrous ammonium sulphate used by 3.25.

Details of this calculation are given under the Analysis of Lead Ores.

Deduct the lead found as lead sulphate from the total lead and calculate the residual lead to PbO.

ZINC.

Boil one gram of the sample in a beaker with the following solution:

Water .....30 c.c.
Ammonium chloride .... 4 grams.
Concentrated hydrochloric acid ..... 6 c.c.

If the sample is not quite dissolved the result is not affected, as the residue is lead sulphate or precipitated lead chloride.

Dilute to 200 c.c. with hot water, add 2 c.c. of a saturated sodium hyposulphite solution and titrate with a standard solution of potassium ferrocyanide, spotting out on a 5 per cent. solution of uranium nitrate as outlined under the Analysis of Lead Ores. Calculate the zinc to zinc oxide.

SULPHUR DIOXIDE.

Digest two grams of the sample with frequent stirring in 5 per cent. sulphuric acid for ten minutes in the cold. Add starch indicator and titrate with N/100 iodine solution.

A more accurate method is to add an excess of standard iodine solution to the sample before the addition of the acid and then to titrate the excess of iodine with N/100 sodium thiosulphate solution. Report the sulphur dioxide found directly, as it does not exist as a sulphite, but is instead an apparently occluded gas.

IRON OXIDE.

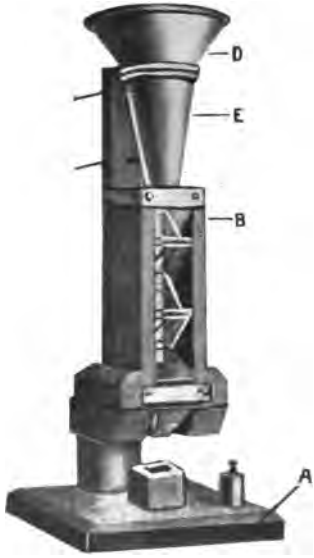
Determine this constituent as outlined under the Analysis of Litharge.

DETERMINATION OF APPARENT DENSITY.

The determination of the apparent density and fineness of lead compounds has lately become of special importance in many laboratories where it is essential that the physical properties of these compounds be under control. The method must combine accuracy and rapidity. While many methods have been suggested for such control, it has been found that when rapidity is required the most excellent results are obtained through the determination of the weight of a cubic inch of the compound. This weight is dependent on two factors, the fineness and the density of the particles.

The determination is carried out on a Scott volumeter, modified by replacing the funnel having a fixed wire screen, with a funnel having an elongated neck, so arranged as to allow the use of various mesh silk bolting cloth. While not only allowing of numerous determinations on fineness, the difficulty encountered through particles of the compound adhering to the wire screen is eliminated.

The apparatus consists of a stand, A, on which is mounted a small tower, B, containing baffle plates of glass which serve to evenly distribute the compound under examination. The funnel is divided into two sections, one the funnel proper,



Modified Form of Scott Volumeter.

D, and the other the neck, E, which fits over the funnel proper and holds the silk bolting cloth firmly in place. The metallic cube is exactly one cubic inch in size.

The mesh cloth most suitable for the compound on which the determination is being made is fastened in the funnel. It has been found that a 72-mesh cloth gives concordant results, it being of such coarseness as, in most cases, to allow all the compound to be brushed through the cloth. The cube is placed directly under the baffle plates, the compound is placed into the funnel and gently brushed through until the cube is entirely filled. By a rapid stroke with a spatula the excess of the compound is removed, leaving an even cubic inch of the material. The cube and its contents are then weighed and the weight of the cube deducted, giving the weight of a cubic inch of the compound. Several determinations should be made and an average should be taken. Results may be obtained by this method which vary not more than ½ of a gram. In the hands of different analysts it has been found that results may vary more than this, due to the personal equation in the carrying out of the method; however, the method is only a comparative one and enables any analyst to closely check the apparent density of compounds in a very rapid manner.

SUBLIMED BLUE LEAD.

Sublimed blue lead is at the present time finding its greatest value as an inhibitive pigment for the protection of iron and steel. The high rating given to this pigment on exposure tests conducted under the supervision of the American Society for Testing Materials for the prevention of corrosion is bringing it more and more to the attention of paint technologists and engineers.

In composition it consists of lead sulphate, lead sulphide, lead sulphite, lead oxide and zinc oxide, with occasional traces of carbon. Its color is a pleasing dull steel gray.

ANALYSIS.

TOTAL LEAD.

The total lead content is determined volumetrically as outlined under the estimation of Lead in Lead Ores.

TOTAL SULPHUR.

Treat one-half gram of the sample in a beaker with 10 c.c. of water and a few c.c. of bromine water. Boil gently until all the bromine has passed off. Dilute with water, add another portion of bromine water, boil and continue the treatment until the sediment has become white in color. Add 8 c.c. of nitric acid, evaporate the solution

until the brown fumes of nitric acid have disappeared, dilute with water and add an excess of sodium carbonate. From this point proceed with the determination of the sulphate as outlined under Sublimed White Lead.

LEAD SULPHATE.

On a separate sample determine the lead sulphate as outlined under Sublimed White Lead, by transposition of the sulphate with sodium carbonate.

LEAD SULPHITE.

Boil one and one-half grams of the sample with 3 grams of sodium carbonate, allow to stand, filter and thoroughly wash. To the filtrate add 3 c.c. of bromine water, heat gently to oxidize the sodium sulphite to sulphate and precipitate the sulphate with barium chloride. Filter, wash and weigh in the usual manner. The barium sulphate formed will contain both the sulphur present as sulphate and that present as sulphite converted to sulphate. Deduct the amount present as sulphate and calculate the remainder to lead sulphite.

LEAD SULPHIDE.

Deduct the sulphur present as sulphate and sulphite from the total sulphur and report the difference as lead sulphide.

LEAD CARBONATE.

A small amount of lead may be present as car-

bonate. Determine the carbonic acid present as outlined under Corroded White Lead, and calculate this carbonic acid to lead carbonate.

LEAD OXIDE.

Deduct the lead present as lead sulphate, lead sulphite, lead sulphide and lead carbonate from the total lead and report the difference as lead oxide.

ZINC OXIDE.

Determine the zinc present as outlined under Sublimed White Lead, and report it as zinc oxide.

CARBON AND VOLATILE MATTER.

Ignite the sample in a partially covered crucible at a low heat for two hours. Report the difference as carbon and volatile matter.

RED LEAD AND ORANGE MINERAL.

These two compounds are oxides of lead, of an approximate formula, Pb_3O_4, being probably a combination of lead dioxide and lead monoxide. They are found on the market as milled oxides and flake oxides. In some instances oxides are found which are artificially colored with organic dyes.

The analysis of red lead and orange mineral consists in the determination of the red lead content or the lead dioxide content, moisture, iron, silica, copper and metallic lead. It is also necessary to determine from a physical standpoint the apparent gravity or density, which may be done by determining the weight of a cubic inch of the material, as outlined on page 19.

MOISTURE.

Dry 2 grams of the sample for 2 hours at 105 degrees C. The loss will be moisture.

RED LEAD, OR LEAD DIOXIDE.

Treat 1 gram of the sample in a beaker with 15 c.c. of nitric acid, sp.g. 1.2 (110 c.c. nitric acid, sp.g. 1.42, to 100 c.c. of water). Stir the sample until all trace of red color has disappeared. Add from a calibrated pipette or burette exactly 10 c.c.

of dilute hydrogen peroxide (1 part of 3% hydrogen peroxide to 3.5 parts of water). Add about 50 c.c. of hot water and stir until all the lead dioxide has passed into solution. In the case of some coarsely ground oxides the contents of the beaker may have to be gently heated to effect complete solution. After the oxide has completely passed into solution, dilute with hot water to about 250 c.c. volume and titrate directly with a standard potassium permanganate solution, having an iron value of .005. Titrate to the faint pink permanganate color. A blank titration on the hydrogen peroxide solution must now be made.

TITRATION OF HYDROGEN PEROXIDE, AND CALCULATION OF RESULTS.

Into a beaker pour 15 c.c. of nitric acid having the strength as above given and add exactly the same amount of hydrogen peroxide (10 c.c.). Dilute to 250 c.c. with hot water and titrate with standard potassium permanganate to a faint pink color.

The difference between the number of c.c. of potassium permanganate required for the blank titration and the number required for the red lead titration is the amount of potassium permanganate required for the hydrogen peroxide which was reacted on by the lead dioxide. The difference between the two amounts of potassium permanganate required multiplied by 3.058 gives

the percentage of red lead present according to the following proportion:

$$2\,Fe : Pb_3O_4 :: .005 : X$$
$$112 : 685 :: .005 : X$$
$$X \text{ equals } 3.058$$

To determine the lead dioxide present multiply this difference by 1.067 according to the following proportion:

$$2\,Fe : PbO_2 :: .005 : X$$
$$112 : 239 :: .005 : X$$
$$X \text{ equals } 1.067$$

FLAKE RED LEAD.

In certain instances it is found that flake red lead is soluble only with the greatest difficulty by the above procedure. In cases where this difficulty is encountered the following method will be found to give excellent results:

Digest 1 gram of the sample in a beaker with 15 c.c. of nitric acid made up of a strength as given in the previous method. Boil the solution for a short time, add 10 c.c. of a standard oxalic acid solution, the strength of which has been previously determined. Add 2 c.c. of sulphuric acid (1:1). Boil the solution and titrate with a standard solution of potassium permanganate having an iron value of .005. A blank titration on the same amount of oxalic acid must be made. The

difference between the amount of potassium permanganate required for the blank titration and that required for the red lead titration multiplied by the factor 3.058 or 1.067 will give the content of red lead or lead dioxide according to the proportions in the previous analysis.

IRON†

This occurs in such a small proportion in all the red leads placed upon the market at the present time that it can best be estimated colorimetrically. Excellent results can be obtained for the colorimetric determination of this constituent by modifying the method of Thomson.* The very slight quantities of copper which sometimes are found do not interfere with the reaction.

One gram of the sample is treated with 10 c.c. of water and just sufficient nitric acid added drop by drop to convert all the oxide present, excepting the lead dioxide, into lead nitrate. Add 10 c.c. of dilute hydrogen peroxide (1:3.5), cover the beaker with a watch glass and boil for a minute to effect complete solution and to convert all the iron to the ferric condition. Wash the contents of the beaker into a 100 c.c. Nessler cylinder, allow the solution to cool, add 15 c.c. of dilute ammonium sulphocyanide solution (1:20), and

†J. I. & E. C., 1912, Sept., ppg. 659.
*J. C. S., 1885, 493.

dilute to mark. The intensity of the red color depends upon the amount of iron present. This color is now compared with a blank carried out in the following way:

For the blank titration a solution of ferric ammonium sulphate of known strength is required. This is made by dissolving .7022 gram of ferrous ammonium sulphate in water. Add 10 c.c. of sulphuric acid, heat to boiling and add a solution of potassium permanganate until the iron is converted to the ferric condition. Only the very slightest pink tinge due to potassium permanganate may be present, as this pink tinge will fade away, while the presence of any pink color will tend to vitiate the results. Allow the solution to cool and dilute to exactly 1 liter. One c.c. of this solution equals .0001 grams of iron. Prepare a blank by placing into a Nessler cylinder 10 c.c. of hydrogen peroxide solution of the above given strength, approximately the same number of drops of nitric acid and 15 c.c. of ammonium sulphocyanide solution. Dilute to 100 c.c., titrate to the exact color developed in the sample of red lead under examination by the addition of the standard ferric ammonium sulphate solution. One c.c. of this solution will equal .01 per cent. of iron when a 1 gram sample is used. It will be found that this method is not only rapid, but that the color can be compared to within .001 per cent. of iron content.

COPPER.

This constituent is best determined gravimetrically, as the very slight percentage of other impurities present in red lead tend to interfere in colorimetric methods.

Twenty grams of the sample are treated in a large beaker with 50 c.c. of nitric acid, 25 c.c. of water and sufficient hydrogen peroxide to cause complete solution of the lead dioxide.

Determine the copper as outlined under the Analysis of Litharge.

SILICA.

Silica is found to be present in oxides of lead both as free silica and as lead silicate, though usually in inappreciable amounts.

Digest 2 grams of the sample in a casserole with 2 grams of potassium chlorate and 15 c.c. of dilute nitric acid. Proceed from this point as outlined under the Analysis of Litharge.

ORGANIC COLOR.

The adulteration of red lead and orange mineral with organic coloring matter may be detected by adding 20 c.c. of 95 per cent. alcohol to 2 grams of the oxide, heating to a boil and allowing to settle. Pour off the supernatant liquid, boil with water, allow to settle and add a very small amount of ammonium hydroxide. If either the alcohol, water or ammonium hydroxide are colored, it indicates organic coloring matter. The quantitative determination is exceedingly difficult and the organic color is usually estimated by difference.

LITHARGE.

Litharge, the monoxide of lead, PbO, may contain small percentages of iron, copper, silica, silver and free metallic lead. When the litharge has been made by a process where steam is used, there may be an appreciable amount of moisture present. It appears on the market in two colors, yellow and red. In some instances litharge is found containing a comparatively large percentage of red lead, which in certain uses is undesirable. The determination of each of the foreign constituents in litharge depends largely upon the use to which the litharge is to be put, as in very few cases are all the constituents determined.

ANALYSIS.

MOISTURE.

Dry 2 grams of the sample at 105° C. for two hours. The loss will be moisture.

FREE METALLIC LEAD.

Two grams of the sample are treated in a beaker with hot water and just sufficient acetic acid is slowly added, to dissolve the lead oxide. Stir the solution well and note whether any lead sili-

cate remains undissolved. Should such remain, continue stirring until solution has been effected. The solution should never have greater than a 5 per cent. acetic acid strength.

Filter the solution and wash the residual metal three or four times by decantation with hot water, having all the wash water pass through the filter paper, which is finally thoroughly washed with hot water. Transfer any metal on the filter paper to the beaker containing the residual lead, add 1 c.c. of concentrated nitric acid and heat to solution. Dilute with 50 c.c. of water, add 1 gram of sodium acetate and follow this with an excess of saturated neutral potassium bichromate solution, sufficient to precipitate all the lead. Boil, dilute to 100 c.c., allow to cool, filter off the lead chromate, wash thoroughly and determine the lead chromate gravimetrically by drying at 100° C. or volumetrically by titration of the chromic acid present as outlined under the Analysis of Lead Ores. The factor for the direct determination of lead is, however, in this case 1.63, as a 2-gram sample is used.

RED LEAD.

Determine the percentage of red lead present as outlined under the Analysis of Red Lead.

IRON.

Treat 1 gram of the sample with 10 c.c. of water and just sufficient nitric acid, added drop by

drop, to cause complete solution. Heat to boiling to oxidize all the iron and determine it colorimetrically as outlined under Red Lead.

COPPER.

Twenty grams of the litharge contained in a 200 c.c. flask are dissolved in nitric acid (50 c.c. concentrated nitric acid to 100 c.c. water). Boil to complete solution. Add 40 c.c. of dilute sulphuric acid (1:1), boil gently for one hour and allow to cool. Filter off the lead sulphate and wash the precipitate thoroughly. Nearly neutralize all the free acid present with ammonium hydroxide, render slightly acid with hydrochloric acid, warm the solution and pass in hydrogen sulphide until no further precipitation of sulphide occurs. Filter off the precipitate without washing, using some of the filtrate to transfer the last traces of sulphide to the filter paper. Dissolve the precipitate in a little nitric acid and wash the filter paper thoroughly with hot water. Add 3 c.c. of concentrated sulphuric acid, evaporate until the white fumes of sulphuric acid are evolved and allow the solution to cool. Add a little water and allow to stand for some hours. Filter off the lead sulphate, washing with hot water containing a little sulphuric acid.

Heat the filtrate to boiling and precipitate the copper as sulphide with hydrogen sulphide in an ammoniacal solution. Filter off the copper sul-

phide through an ashless filter paper, wash, ignite and weigh in a covered porcelain crucible, from which the heat and cover are occasionally removed for a few seconds.

The precipitate will consist of a mixture of CuO and Cu_2S. Since the percentage of copper is the same in both of these, the copper may be determined by multiplying the amount found by the factor .7988.

SILICA.

Digest 5 grams of the sample in a covered casserole with 2 grams of potassium chlorate and 15 c.c. of dilute nitric acid (1:1). Evaporate to dryness and dehydrate. Treat the residue, after cooling, with hot water and nitric acid. Heat to boiling, and filter the solution through an ashless filter paper. Wash the residue and filter paper thoroughly with hot acid ammonium acetate solution, made up to a strength as outlined under the Analysis of Lead Ores. Should the residue show a trace of iron, wash it thoroughly with dilute hydrochloric acid. Complete the washing with hot water, dry, ignite and weigh as SiO_2. The residue may be volatilized with hydrofluoric acid, if there is any doubt regarding the purity of the silica.

The silica is present as lead silicate and free silica. The above method determines the total content of silica. The free silica may be determined by dissolving the litharge in dilute nitric acid. Heat to boiling, filter, wash, ignite and weigh as silica.

BASIC CARBONATE OF LEAD.

(Corroded White Lead.)

Basic carbonate white lead ($2PbCO_3Pb(OH)_2$) contains approximately 80 per cent. metallic lead and 20 per cent. carbonic acid and combined water, with traces of silver, antimony, lead, and other metals. The analysis of basic carbonate white lead can best be carried out by Walker's method.

(A) TOTAL LEAD.

"Weigh 1 gram of the sample, moisten with water, dissolve in acetic acid, filter, wash, ignite, and weigh the insoluble impurities. To the filtrate from the insoluble matter add 25 c.c. of sulphuric acid (1:1), evaporate and heat until the acetic acid is driven off; cool, dilute to 200 c.c. with water, add 20 c.c. of ethyl alcohol, allow to stand for two hours, filter on a Gooch crucible, wash with 1 per cent. sulphuric acid, ignite, and weigh as lead sulphate. Calculate to total lead ($PbSO_4 \times 0.68292 = Pb$) or calculate to basic carbonate of lead (white lead) by multiplying the weight of lead sulphate by 0.85258.

"The filtrate from the lead sulphate may be used to test for other metals, though white lead is

*P. H. Walker, Bureau of Chemistry Bulletin No. 109, revised, U. S. Dept. of Agriculture, pp. 21 and 22.

only rarely adulterated with soluble substances; test, however, for zinc, which may be present as zinc oxide.

"Instead of determining the total lead as sulphate it may be determined as lead chromate by precipitating the hot acetic acid solution with potassium bichromate, filtering on a Gooch crucible, igniting at a low temperature, and weighing as lead chromate.

(B) COMPLETE ANALYSIS.

"When it is necessary to determine the exact composition of a pure white lead, heat 1 gram of the pigment in a porcelain boat in a current of dry, carbon-dioxide-free air, catching the water in sulphuric acid and calcium chloride and the carbon dioxide in soda lime or potassium hydroxide (1.27 specific gravity). By weighing the residue of lead monoxide in the boat all the factors for determining the total composition are obtained. Figure the carbon dioxide to lead carbonate ($PbCO_3$), calculate the lead monoxide corresponding to the lead carbonate ($PbCO_3$) and subtract from the total lead monoxide, calculate the remaining lead monoxide to lead hydroxide ($Pb(OH)_2$), calculate the water corresponding to lead hydroxide and subtract from the total water, the remainder being figured as moisture.

*J. Soc. Chem. Ind., 1905, 24:487.

"This method assumes the absence of acetic acid. Thompson* states that acetic acid varies from 0.05 per cent. in Dutch process white lead to 0.7 per cent. in some precipitated white leads. It is then more accurate to determine the carbon dioxide by evolution; this is especially the case when working with a lead extracted from an oil paste, as the lead soap and unextracted oil will cause a considerable error by the ignition method. In determining carbon dioxide by the evolution method, liberate the carbon dioxide with dilute nitric acid, have a reflux condenser next to the evolution flask and dry the carbon dioxide with calcium chloride before absorbing it in the potassium hydroxide bulbs.

(c) ACETIC ACID.

"It is sometimes necessary to determine acetic acid. The Navy Department specifications demand that white lead shall not contain 'acetate in excess of fifteen one-hundredths of 1 per cent. of glacial acetic acid.' Thompson's method* is as follows:

" 'Eighteen grams of the dry white lead are placed in a 500 c.c. flask, this flask being arranged for connection with a steam supply and also with an ordinary Liebig condenser. To this white lead is added 40 c.c. of syrupy phosphoric acid, 18

*J. Soc. Chem. Ind., 1905, 24:487.

grams of zinc dust, and about 50 c.c. of water. The flask containing the material is heated directly and distilled down to a small bulk. Then the steam is passed into the flask until it becomes about half full of condensed water, when the steam is shut off and the original flask heated directly and distilled down to the same small bulk—this operation being conducted twice. The distillate is then transferred to a special flask and 1 c.c. of syrupy phosphoric acid added to insure a slightly acid condition. The flask is then heated and distilled down to a small bulk—say, 20 c.c. Steam is then passed through the flask until it contains about 200 c.c. of condensed water, when the steam is shut off and the flask heated directly. These operations of direct distillation and steam distillation are conducted until 10 c.c. of the distillate require but a drop of tenth-normal alkali to produce a change in the presence of phenolphthalein. Then the bulk of the distillate is titrated with tenth-normal sodium hydroxide, and the acetic acid calculated. It will be found very convenient in this titration, which amounts in some cases to 600-700 c.c., to titrate the distillate when it reaches 200 c.c., and so continue titrating every 200 c.c. as it distils over.

"If the white lead contains appreciable amounts of chlorine it is well to add some silver phosphate to the second distillation flask and not carry the

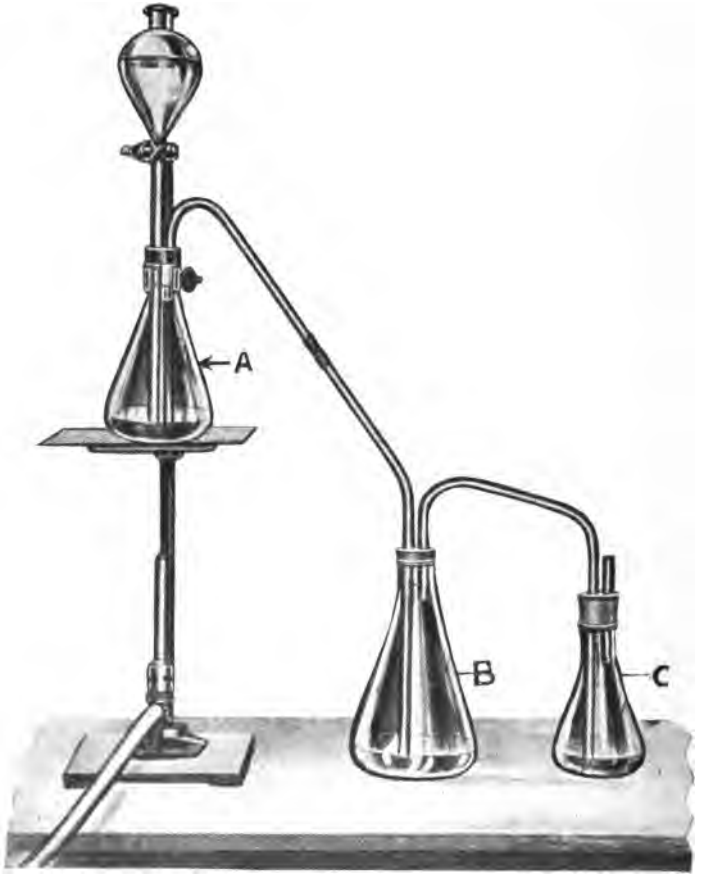
distillation from this flask too far at any time.

"The method used by the chemists of the Navy Department is as follows: Weigh 25 grams of white lead in an Erlenmeyer flask, add 75 c.c. of 25 per cent. phosphoric acid, distil with steam to a 500 c.c. distillate, add to the distillate some milk of barium carbonate, bring to a boil, filter, keeping the solution at the boiling point (it is not necessary to wash), add an excess of sulphuric acid to the filtrate and determine the barium sulphate in the usual manner; subtract 53 milligrams from the weight of the barium sulphate and calculate the remainder as acetic acid ($BaSO_4$ times 0.515 equals CH_3COOH). The object of this rather indirect method is to avoid any error that might arise from fatty acids being carried over by the steam distillation. For white lead that has not been ground in oil, Thompson's method is to be preferred."

(D) CARBONIC ACID.

The carbonic acid content of white lead may be determined by using the Scheibler apparatus, complete reference to which, with all tables, may be found in "The Analysis of Paints and Painting Materials,"* page 6. A more simple and efficacious method of determining the carbonic

*The Analysis of Paints and Painting Materials, Gardner and Schaeffer: The McGraw-Hill Book Company, New York.



Carbon Dioxide Apparatus.

acid content will be found in the following method:

The method can be used in such cases where the substances to be analyzed evolve gases other than carbon dioxide; that is, hydrogen sulphide, sulphur dioxide, or organic matter. The apparatus used is shown in the accompanying diagram. A weighed sample of the substance is introduced into the Erlenmeyer flask (A). Into flask (B) is placed a 10 per cent. solution of barium chloride, more than sufficient to hold the carbon dioxide evolved, and 20 c.c. of concentrated ammonium hydroxide free from carbon dioxide. If sulphides are present, it is sometimes advisable to pass the liberated gas first through a few c.c. of strong potassium permanganate. The flask (B) is warmed until completely filled with ammonia fumes. Flask (D) is a safety bottle containing the same solution as flask (B). Only in rare cases will any trace of carbon dioxide be noticed in the safety flask. After flask (B) is completely filled with ammonia vapor, make all connections and allow the hydrochloric acid to drop slowly from the separatory funnel into the decomposition flask (A). When effervescence has ceased, heat the contents of the flask until filled with steam. The delivery tubes and sides of the precipitating flask are then washed with boiling water, the flask is filled to the neck, stoppered, and the precipi-

tated barium carbonate allowed to settle. Wash thoroughly by decantation, each time stoppering the flask to prevent any error from the carbon dioxide present in the air, and determine either gravimetrically, by conversion into barium sulphate, or volumetrically, by dissolving in standard hydrochloric acid and titrating the excess of acid used with standard potassium hydroxide. Calculate the barium found to carbonate and the amount of carbon dioxide from the found carbonate. The entire operation may be hastened by conducting a brisk current of air free from carbon dioxide through the entire apparatus.

Two new and rapid volumetric methods for the determination of carbonic acid contents are described in detail by Leon T. Bonser in the *Journal of Industrial and Chemical Engineering,* March, 1912, page 203, and by H. W. Brubaker in the same journal, August, 1912.

A few typical analyses of basic carbonate white lead, for impurities, are given:

TYPICAL ANALYSES OF BASIC CARBONATE WHITE LEAD FOR IMPURITIES.

Insoluble	.0252	.0130	.0241	.0417	.0089	.0307	.0123	.0594
Antimony	.0019	.0085	0035	.0028	.0031	.0074	.0054	.0080
Arsenic	.0001	.0072	.0010	.0024	.0022	.0027	.0018	.0008
Bismuth	.0197	.0165	.0122	.0209	.0329	.0226	.0395	.0133
Silver	none	none	none	none	none	none	none	none
Cadmium	none	none	none	none	none	none	none	none
Copper	.0005	trace	.0014	.0012	.0013	.0008	.0006	.0111
Nickel	none	trace	trace	none	none	none	trace	none
Zinc	0008	.0005	.0006	.0008	.0009	.0003	.0005	.0003
Manganese	none	none	none	none	none	none	none	none
Calcium	.0300	.0057	.0142	.0071	.0143	.0143	.0100	.0172
Iron oxide	.0038	.0045	.0042	.0035	.0043	.0031	.0035	.0056
Aluminum oxide	.0009	.0005	.0004	.0014	.0001	.004	.0019	.0032
Sulphur trioxide	.0338	.0021	0105	.0049	.0442	.0049	.0099	.0196
Chlorine	.0299	.0497	.0165	.0403	.0149	.0420	.0425	.0118
Acetic acid	.4539	.3157	.3060	.2558	.2558	.5462	.5853	.2681

ELECTROLYTIC DEPOSITION OF LEAD.

Lead may be determined electrolytically in a very rapid manner by following the procedure as outlined by Smith* in his Electro-Analysis.

THE RAPID PRECIPITATION OF LEAD DIOXIDE WITH THE USE OF A ROTATING ELECTRODE.

"Twenty c.c. of concentrated nitric acid were added to a solution of lead nitrate, giving a total volume of about 125 c.c. and acted upon with a current of $N.D._{100} = 10$ amperes and 4.5 volts. The rotating electrode (cathode) performed 600 revolutions per minute. The deposits had a uniform, velvety black color. There was no tendency on the part of the deposit to scale off, though more than a gram of the dioxide was precipitated. The time varied from ten to fifteen minutes. A platinum dish with sand-blasted inner surface was used as anode.

By using a current of $N. D._{100} = 11$ amperes and 4 volts upon a solution of lead nitrate containing 0.4996 gram of lead or 0.5787 gram of dioxide, the rate of precipitation was found to be:

---

*Electro-Analysis, Smith: P. Blakiston's Sons & Co.

In 5 minutes..0.4940 gram lead dioxide.
In 10 minutes..0.5708 gram lead dioxide.
In 15 minutes..0.5747 gram lead dioxide.
In 20 minutes..0.5770 gram lead dioxide.
In 25 minutes..0.5787 gram lead dioxide.
In 30 minutes..0.5789 gram lead dioxide.

The maximum time period for a quarter of a gram of metal is fifteen minutes, and the maximum time for a half gram of metal is twenty-five minutes."

PIG LEAD.

Pig lead is placed upon the market, both in the refined and crude condition. It will usually contain small varying amounts of other metals, such as antimony, arsenic, bismuth, cadmium, copper, iron, manganese, nickel, cobalt, silver and zinc.

Refined lead and crude lead are analyzed by the same procedure, save that a 200-gram sample of refined lead is usually required, while a 20-gram sample of the crude lead is ample in most cases. The following methods deal with the analysis of crude lead, for the analysis of refined lead proportionally larger volumes and weights are used.

ANALYSIS.

The lead is carefully scraped with a bright knife until a clean surface is exposed. The requisite amount of lead is removed either by cutting off comparatively large pieces with a knife or by filing off small particles with a bright, clean file. Treat the sample with warm dilute hydrochloric acid, wash thoroughly with hot water and dry, so as to insure the removal of all foreign adhering impurities.

Weigh off exactly 20 grams and transfer the same to a 500 c.c. Erlenmeyer flask. Add 50 c.c.

of concentrated nitric acid and sufficient water (about 25 c.c.) and heat until complete solution has been effected. Add sufficient water (about 60 c. c.) to prevent the separation of any lead nitrate. In certain instances where the lead contains a high percentage of antimony a white precipitate may remain. When this occurs, it is removed by filtration and washing. The precipitate is reserved for further treatment.

Add 20 c.c. of concentrated sulphuric acid, diluted with water, to the clear lead solution. Boil the solution gently until sulphuric acid fumes are evolved, allow to cool, dilute to 250 c.c. with water and filter off the precipitated lead sulphate.

In a lead high in antimony, the lead sulphate precipitate may be contaminated with antimony. In this case the lead sulphate is dissolved in hydrochloric acid, diluted with water and treated with hydrogen sulphide. The precipitated sulphides are filtered and treated with yellow ammonium sulphide to dissolve any antimony sulphide present. The insoluble lead sulphide is removed by filtration. The residue, should any such have remained, obtained in the original solution of lead in nitric acid is added to the filtrate and the combination of the two reserved for future treatment.

Warm the filtrate from the lead sulphate precipitation after adding ammonium hydroxide un-

til the greater portion of the free acid has been neutralized, to about 80° C. and treat with hydrogen sulphide until no further precipitation occurs. Filter off the precipitated sulphides and wash with hydrogen sulphide water.

The filtrate will contain the iron, nickel, cobalt and zinc, while the precipitate will contain the copper, cadmium, bismuth, arsenic, antimony and silver. The later metals are separated according to the method outlined by Fresenius,* the method, however, being slightly modified.

The precipitate is gently heated in a beaker, after complete removal from the filter paper, with yellow ammonium sulphide. Filter off the insoluble sulphides and wash.

Treat the small quantity of precipitate which is insoluble in the yellow ammonium sulphide, after spreading out the filter in a small dish, with diluted nitric acid (1 part nitric acid, sp.g. 1.2, to 2 parts of water), at near the boiling point. When the precipitate has dissolved, filter, wash the filter, dry and incinerate, adding the ashes to the nitric acid solution. Add 2 c.c. of concentrated sulphuric acid, evaporate to sulphuric acid fumes, dilute with a little water and filter off any residual lead sulphate. Nearly neutralize the filtrate

*Quantitative Chemical Analysis, Fresenius, Vol. 2, pages 584-590.

with potassium carbonate, then add sodium carbonate and a little potassium cyanide, free from potassium sulphide, and heat gently. Any precipitated bismuth is filtered off, washed thoroughly, dissolved in dilute nitric acid and determined by precipitation with ammonium carbonate and weighing as oxide or is fused with potassium cyanide and weighed as metal.

The clear filtrate is treated with more potassium cyanide and any cadmium present is precipitated by the addition of a little potassium sulphide. Any silver present will be precipitated with the cadmium, consequently the precipitate is removed by filtration, with subsequent washing, dissolved in hot dilute nitric acid and the silver is precipitated by the addition of a few drops of hydrochloric acid. Filter and evaporate the filtrate almost to dryness and precipitate any cadmium present with sodium carbonate. If any cadmium is precipitated, dissolve it in nitric acid, evaporate, ignite and weigh as cadmium oxide.

To the filtrate from the cadmium and silver sulphides, add a little sulphuric and nitric acids and a few drops of hydrochloric acid and evaporate until the odor of hydrocyanic acid has entirely disappeared. Precipitate the copper in this solution, filtered if not clear, with hydrogen sulphide, filter, wash and weigh the copper as a

mixture of Cu_2S and CuO as stated under the Analysis of Litharge. Before the copper is precipitated the solution must always be tested for silver, to avoid contamination.

The combined solutions containing antimony, as previously stated, and the filtrate obtained from treatment of the sulphides with yellow ammonium sulphide are combined and rendered acid with hydrochloric acid. Filter off the precipitated sulphides. They are examined for arsenic and antimony according to the method of Neher* as follows:

The sulphides are dissolved in a solution of potassium hydroxide and oxidized in a casserole, warmed gently on the water bath, with chlorine until all the alkali is decomposed. This requires from one-half to three-quarters of an hour. Any chlorate is decomposed by adding concentrated hydrochloric acid, drop by drop, to the warm solution until no more chlorine is evolved. "When free from chlorate, the acid solution is washed into an Erlenmeyer flask and cooled by surrounding the flask with ice. In another flask concentrated hydrochloric acid (sp.g. 1.2) is likewise cooled. When both solutions are at 0° C., the arsenic-antimony solution is diluted with twice its

*Zeit. fur Anal. Chemie., 32-45. Translation from Treadwell and Hall's Analytical Chemistry, 183, 184, Vol. 2

volume of the strong hydrochloric acid. Into this cold solution a rapid stream of hydrogen sulphide is passed for one and one-half hours. The flask is stoppered up and allowed to stand one to two hours. The As_2S_5 is filtered through a Gooch crucible and washed with hydrochloric acid (1 vol. water to 2 vol. concentrated hydrochloric acid) until 1 c.c. of the filtrate, after being considerably diluted with water and tested with hydrogen sulphide, shows no precipitation. It is then washed with water, and finally with hot alcohol. After drying at 110° C., the precipitate is weighed as As_2S_5.

"The filtrate from the arsenic sulphide precipitation is diluted largely with water and saturated with hydrogen sulphide. The Sb_2S_5 is filtered through a Gooch crucible, dried at 230° C. and weighed."

IRON, NICKEL, COBALT, MANGANESE AND ZINC.

The filtrate and washings from the hydrogen sulphide precipitation containing the iron, manganese, nickel, cobalt and zinc are rendered alkaline with ammonium hydroxide and treated with ammonium sulphide. Pour the solution into a flask, fill up the flask to the neck, stopper and set aside for at least twenty-four hours and filter. Add acetic acid to the filtrate just to acidity, then ammonium acetate and evaporate at a gentle heat, so that if a trace of nickel sulphide is retained in

the solution it will be precipitated with the sulphur. Collect this sulphur on a filter paper.

Treat the precipitated sulphides on the filter paper repeatedly with a mixture of about 6 parts of hydrogen sulphide water and 1 part of hydrochloric acid (sp.g. 1.2), so that the sulphides may be dissolved with the exception of the nickel and cobalt sulphides. Combine this precipitate with the sulphur precipitate obtained in the above separation and examine them for nickel and cobalt. These sulphides may also be separated by the sodium succinate method as outlined in Treadwell and Hall's Analytical Chemistry.

The filtrate containing the iron, manganese and zinc is concentrated by evaporation and finally with the addition of a little nitric acid. Precipitate with ammonium hydroxide and filter; redissolve the precipitate in hydrochloric acid, again precipitate with ammonia, wash, dry and weigh the iron oxide or determine it volumetrically in the usual way.

The iron may be determined directly in the sample by following the colorimetric method as outlined under the Analysis of Red Lead.

The filtrate from the iron oxide is treated with ammonium sulphide and allowed to stand twenty-four hours at a gentle heat. Filter off any precipitate and treat it with dilute acetic acid to re-

move any manganese sulphide. Determine the zinc gravimetrically or volumetrically as outlined under the Analysis of Lead Ores.

Evaporate the acetic acid solution to a small volume and examine for the presence of manganese.

SILVER.

The silver is best determined by direct cupellation of the requisite amount of metallic lead, this amount depending upon the kind of lead examined.

IODOMETRIC DETERMINATION OF ANTIMONY AND ARSENIC IN LEAD-ANTIMONY ALLOYS.

G. M. Howard* has described a method of separating and determining antimony and arsenic in lead-antimony alloys, which he uses in the laboratory of the Electric Storage Battery Co.

In this method tin does not interfere, making it applicable in the analysis of type metal. Small amounts of iron or copper do not interfere.

"Weigh 0.5 to 2 gram portions of the sample in the form of fine filings into dry 125 c.c. Erlenmeyer flasks. Heat the finely divided alloy (it is a good plan to run the filings through a fairly fine sieve) with HCl until action ceases. Remove the flask from the plate, add about 0.5 c.c. of HNO_3 and let stand a few moments until the reddish color is obtained. Then shake the flask, when the Sb and As will dissolve quickly and completely. Now place upon the plate again and boil vigorously for five minutes or so.

"Now, while still hot, pass hydrogen sulphide into the solution until it is completely saturated; 15 minutes is usually sufficient. If insufficient

*J. A. C. S., 30, 378 (1908).
*C. A., 2, 2348.
*J. A. C. S., 30, 1789-90.

hydrochloric acid has been used, or the solution has been boiled so long on the hot plate that much has been lost, antimony sulphide will be precipitated as the solution cools.

"The hydrogen sulphide treatment is most conveniently handled by fitting the flasks with two-hole stoppers and inlet and outlet tubes, and connecting several in series to the generator. If the outlet in the last flask is led into a bottle of caustic soda solution, no gas escapes into the room. When saturated the flasks are transferred to a current of air, still in series and again absorbing the gas from the last flask in the caustic soda, and the air passed until all of the hydrogen sulphide is removed (one-half hour is sufficient for two flasks). The hydrogen sulphide precipitates nothing but arsenic as sulphide, but reduces all salts capable of reduction, antimony, tin, copper, iron, etc. The current of air then reoxidizes all these except the antimony, which remains in the antimonious form.

"To the now cold solution add a little tartaric acid, and enough water to double the bulk, and filter through a double filter into a one-half litre flask. Practically all of the lead chloride must be washed out of the precipitate with hot water, but it is not necessary to add all of the washings to the filtrate, as the antimonious chloride is readily washed out by decantation with cold water.

"The filtrate is nearly neutralized by adding powdered sodium carbonate in small portions, care being used not to reach the point of precipitation of the lead, or, if this is reached, making it slightly acid again with hydrochloric acid. The neutralization is then completed with sodium bicarbonate and a slight excess added (about one teaspoonful of powder). The antimony is then determined by titrating with standard iodine solution, using fresh starch solution as indicator. The precipitate of lead carbonate does not affect the titration, and with a little practice the end point can be recognized just as easily as in a clear solution. Too much starch should be avoided, as it makes the end point obscure. A convenient strength for the iodine solution is 1 c.c. = 0.005 gram antimony, then with a 0.5 gram sample, 1 c.c. = 1% antimony.

"If arsenic is negligibly low, which, with a little experience, can be pretty well gauged by the appearance of the precipitate, or for any reason is not to be determined, the filtering may be dispensed with. In this case the whole solution, with the arsenious sulphide, if any, and free sulphur in suspension, is merely transferred to a larger flask, neutralized and titrated. The suspended arsenious and free sulphur are without effect."

"The bulk of the arsenious sulphide and sulphur is washed off the filter back into the same flask in which the precipitation was made, using not more than 20 c.c. or so of water. A few drops of sodium hydroxide are added (5 drops of 20 per cent. solution is ample), the solution boiled for a few moments and then decanted through the filter into a 250 c.c. Erlenmeyer flask. This weak soda readily dissolves the arsenious sulphide, while taking up only a small part of the free sulphur. If the amount of precipitate is at all considerable, it is safer to give a second treatment with soda solution.

"The filter is washed with hot water and discarded. To the filtrate is added hydrogen peroxide solution, which should be reasonably fresh, or else its strength known. Twenty c.c. of 3 per cent. solution is sufficient for arsenic up to several per cent. The hydrogen peroxide oxidizes all arsenic and also all sulphur compounds, giving a colorless solution. This is now boiled down to a small bulk, about 20 c.c., the excess of peroxide being decomposed in the process. When cool, potassium iodide solution is added in amount equivalent to about 0.1 gm. of KI, then 20 c.c. of concentrated hydrochloric acid. After standing five minutes it is cooled and titrated with standard thiosulphate, adding three drops of starch solu-

tion only when the color is almost gone. A convenient strength for the thiosulphate solution is 1 c.c. = 0.001 gm. arsenic, and it should, of course, be frequently standardized. It is well also to run a blank titration, using the same amounts of reagents as in the analysis, to determine whether there is any constant to be deducted from the burette reading, due to impurities in the reagents. The difficulty with the end point experienced by many in this titration appears to be due to the use of too large an excess of KI and too much starch. With the proportions given above, the end point is exceedingly sharp, and the reaction seems to be just as complete as when more KI is added."

Index.

A.

Page

Acetic acid, in basic carbonate of lead..... 37
Thompson's method 37
Navy method 37
Antimony, in lead—antimony alloys..... 56
Antimony, in pig lead..... 51
Apparent density, determination of..... 19
Ammonium molybdate method for lead..... 8
Arsenic, in lead—antimony alloys..... 57
Arsenic, in pig lead..... 51

B.

Basic carbonate of lead, analysis of..... 35
Basic carbonate of lead, composition of..... 35
Basic sulphate of lead, analysis of..... 15
Basic sulphate of lead, composition of..... 15
Bismuth, in pig lead..... 49

C.

Cadmium, in pig lead..... 49
Carbon, in sublimed blue lead..... 24
Carbonic acid, in basic carbonate of lead..... 39
Carbonate of lead, in sublimed blue lead..... 23
Cobalt, in pig lead..... 52
Copper, in litharge..... 33
in pig lead..... 49
in red lead..... 30
Corroded white lead, analysis of..... 35

E.

Electrolytic deposition of lead..... 44

F.

Flake red lead, analysis of..... 27

H.

Howard method for iodometric determination of antimony and arsenic in lead—antimony alloys 54

I.

Iodometric method for the determination of antimony and arsenic in lead—antimony alloys... 54
Iron—in litharge 32
in orange mineral 28
in pig lead..... 52
in red lead 28
in sublimed white lead 18

L.

Lead, bichromate method for..... 9
Lead, in lead ores..... 7
Lead, in sublimed blue lead..... 22
Lead, in sublimed white lead—
bichromate method 17
molybdate method 16
sulphate method 16
Lead, molybdate method for..... 7
Lead, metallic, in litharge..... 31
Lead oxide, in sublimed blue lead..... 24
Lead oxide, in sublimed white lead..... 17
Lead oxide in red lead and orange mineral..... 25
Lead sulphide, in sublimed blue lead..... 23
Lead sulphite, in sublimed blue lead..... 23
Lead sulphate, in sublimed white lead..... 16
Lead sulphate, in sublimed blue lead..... 23

Lead, total, in basic carbonate of lead..... 35
Lead, total, in sublimed white lead..... 16
Litharge, analysis of..... 31
Litharge, composition of..... 31

M.

Manganese, in pig lead..... 53
Moisture, in litharge..... 31
in red lead..... 25
Molybdate method for volumetric determination of lead 8

N.

Nickel, in pig lead..... 52

O.

Orange mineral, analysis of..... 25
Organic color, in orange mineral..... 30
in red lead 30
Orange mineral, composition of..... 25

P.

Pig lead, analysis of..... 46
Potassium bichromate method for volumetric determination of lead 9
Potassium ferrocyanide method for volumetric determination of zinc 11

R.

Red lead, analysis of 25
Red lead content, determination of..... 25
in litharge 32
in orange mineral 25
in red lead 25
Red lead, composition of..... 25

S.

Scott volumeter 20
Silica, in litharge 34
in red lead 30
Silver, in lead ores 13
in pig lead 49
Smith's method for electrolytic deposition of lead. 44
Sublimed blue lead, analysis of 22
Sublimed white lead, analysis of 15
Sublimed blue lead, composition of 22
Sublimed white lead, composition of 15
Standardization of ammonium molybdate for determination of lead 8
Standardization of potassium ferrocyanide for determination of zinc 12
Sulphate, lead, in sublimed blue lead 23
Sulphate, lead, in sublimed white lead 15
Sulphate method, for lead 35
Sulphite, lead, in sublimed blue lead 23
Sulphate, lead, in sublimed blue lead 23
Sulphur, total, in sublimed blue lead 22
Sulphur dioxide, in sublimed white lead 18

T.

Thompson's method for acetic acid 37
Total lead, in sublimed blue lead 22
Total lead, in sublimed white lead 16
Total sulphate, in sublimed blue lead 22
Total sulphate, in sublimed white lead 15
Typical analyses of basic carbonate of lead 43

V.

Volatile matter, in sublimed blue lead 24

Volumetric methods for lead—
Bichromate method 9
Molybdate method 8
Volumetric method for zinc—ferrocyanide method 11

W.

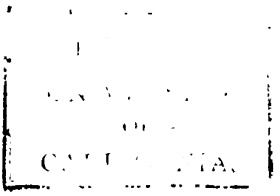
Walker's method, for basic carbonate of lead..... 35

Z.

Zinc, in lead ores 11
Zinc, in pig lead..... 52
Zinc oxide, in sublimed white lead..... 17
Zinc oxide, in sublimed blue lead..... 24
Zinc, potassium ferrocyanide method for..... 11

UNIV. OF
CALIFORNIA

UNIV. OF
CALIFORNIA



RETURN TO the circulation desk of any
University of California Library
or to the
NORTHERN REGIONAL LIBRARY FACILITY
Bldg. 400, Richmond Field Station
University of California
Richmond, CA 94804-4698

ALL BOOKS MAY BE RECALLED AFTER 7 DAYS
2-month loans may be renewed by calling
(415) 642-6233
1-year loans may be recharged by bringing books
to NRLF
Renewals and recharges may be made 4 days
prior to due date

DUE AS STAMPED BELOW

NOV 28 1988
OCT 5 1990

YB 66867